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t: RIGIDIZED INFLATABLE SOLAR ENERGY CONCENTRATORS

by

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FOURTH MONTHLY PROGRESS REPORT,

COVERING PERIOD FROM 1 JANUARY ~~THROUGH~~ 31 JANUARY 1963

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I. INTRODUCTION

This report covers the work accomplished from 1 January 1964, through 31 January 1964.

Measurements have been made for the chemical and physical properties of the available azides. Studies have been made of the formulation variations and their effects upon strength and temperature. A Vicat softening apparatus has been constructed to aid in these investigations. Azotometer, heat of rearrangement, and sublimation tests have been performed for most of the available materials. Some of the data obtained indicates that a near optimum azide material may have been obtained. Greater consideration in the area of prepolymerization is expected to offer an improved material reaction.

The preparation of design goals are in process. They will probably be included in the next monthly report.

A revised schedule is presented in Figure 1 which shows an extension of the foam formulation effort.

AUTHOR

II. WORK ACCOMPLISHED DURING THIS REPORTING PERIOD

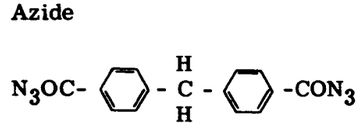
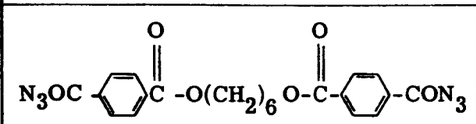
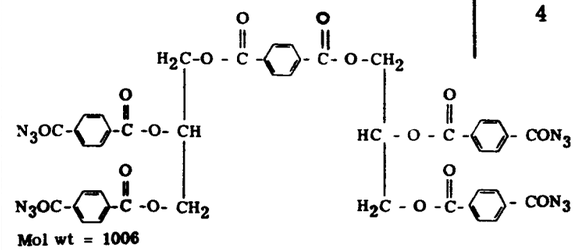
A. Azide Materials

A recapitulation of structures and properties of azide Structures I, X, XI and XII is shown in Table A. Extensions have been made with respect to melting points for X and XI (supplier's determinations) and calorimetric determinations of heats of rearrangement for the same structures.

A summary of information on the rate of azide rearrangement at constant temperature for Structures I, X and XI is contained in Table B. Results with X seem acceptable in view of the probable experimental errors in initial work with the azotometer. However, the results with I and XI suggest these materials may be of low purity (less than 90% pure) or that they do not undergo a near quantitative rearrangement reaction to the desired isocyanates. Further study is necessary since either source of discrepancy would throw uncertainty into the equivalent weight to be used in precoat formulation.

With the experimental determination of heat releases from the rearrangement reactions of the respective azides, it has been possible to forecast heat releases and resultant adiabatic temperature rises for precoat formulations employing candidate polyol resins and equivalent quantities of the respective azide structures that are being investigated. This is summarized in Table C. Comparison of values of calculated adiabatic temperature rises for the various formulations indicates the desirability of employing as highly pre-polymered a resin as possible to minimize quantity of azide required and resulting heat release.

Table A. Properties of Acid Azides (Continued)

Structure	~~Azide Name~~ and Mol Structure	Azide Functionality	Isocyanate Produced on Rearrangement	Azide N Content (Wt %) Total	Azide N Content (Wt %) Releasable	Azide Melting Point (°F)	Crystal Density of Azide (g/cc)	Half Life** at Stated Temperature (min)	Heat Release on Rearrangement at 275°F (cal/g)	Remarks Pertaining to Azides
I	Terephthaloyl Azide  Mol wt = 216	2	1, 4 -Benzene Diisocyanate	38.9	25.9	230-232	1.58	28 (prelim) at 196°F †	282	--
X	**4, 4' -Diphenyl Methane Diacyl Azide**  Mol ~~wt~~ = ~~306~~	**2**	**4, 4' -Diphenyl Methane Diisocyanate** Mol wt = 250 Amine eq = 125	**27.4**	**18.3**	181-184 (dec.)	**1.34**	**30 (prelim) at 193°F**	224	Have not observed detonation on rapid heating.
XI	 Mol wt = 464	**2**	-- Mol wt = 408 Amine eq = 204	**18.1**	**12.1**	190-199 (dec.)	**1.31**	24 (prelim) at 196° F †	115	Have not observed detonation on rapid heating.
XII	 Mol wt = 1006	**4**	-- Mol wt = 894 Amine eq = 224	**16.7**	**11.1**	--	--	--	--	No authentic material yet available.

**Assuming a unimolecular reaction, the time for 50 percent of the material to undergo rearrangement as measured by nitrogen release.
† Experimental value adjusted for suspected low purity.

TABLE B

Azide Decomposition Rates[a] - Azotometer Measurements

	Structure I		Structure X		Structure XI	
Temperature (°F)	196	207	193	208	196	208
Time (minutes) for following per cent decompositions:[b]						
25%	---	---	12	5	---	---
50%	28	13	30	11.5	24	10
75%	---	---	66	23	---	---

The above data are preliminary, but serve the immediate purpose of establishing the rate of azide rearrangement versus temperature relationship.

(a) For data analysis the following purities are tentatively assumed from internal and related evidence:

Structure I - 83%
Structure X - 100%
Structure XI - 85%

(b) Times are read from plotted curves of gas production versus run time; a correction is applied for hold up in the system leading to an apparent induction period.

Table C. Relationships in Formulating Azides with Polyol Resins

Resin	PFR-6 (Hydroxyl No. = 480)			Voranol RS-375 (Hydroxyl No. = 375)			HP-370 (Hydroxyl No. = 370)			Prepolymer from 10 pbw PFR-6 + 2.3 pbw Glidfoam RCR-5043 (Hydroxyl No. = ~304)		
	100(pbw)	100(pbw)	100(pbw)	100(pbw)	100(pbw)	100(pbw)	100(pbw)	100(pbw)	100(pbw)	(100(pbw)	100(pbw)	100(pbw)
Azide Component (for -NCO/OH = 1)												
Structure I	92/192	--	--	71.5/171.5	--	--	72/172	--	--	58/158	--	--
Structure X	--	131/231	--	--	101/201	--	--	102/202	--	--	83/183	--
Structure XI	--	--	198/298	--	--	153.5/253.5	--	--	155/255	--	--	125/225
Weight after Azide Rearrangement	168	207	274	153	182.5	235	153	183	236	143	168	210
Calculated Mol Wt /Cross Link (M_c)	†	†	†	308	367	473	459	549	708	†	†	†
Vol N_2(STP)/Vol Polyurethane Solids (Calculated)*	136	111	84	116	97	76	119	100	77	102	87	69
Adiabatic Temp Rise from Azide Rearrangement - °F (Calculated)**	617	565	333	528	495	300	532	498	302	457	441	273

*Assuming for polyurethane solids, d = 1.2 g/cc

**Based on material weight after rearrangement, material specific heat of 0.45 cal/g-°C (assumed) and azide heat releases as follow: Structure I - 282 cal/gm, Structure X - 224 cal/gm, Structure XI - 115 cal/gm.

† Information on average functionality of PFR-6 is not available at present.

TABLE D

Subliming Rates of Azides and Resins in High Vacuum

	Per Cent Weight Loss[a] (Accumulated)			
	Structure I	Structure X	Structure XI	MDI[b]
Hours at 75° F:				
17	37	--	--	--
17.5	--	0.3	0.3	--
23	--	--	--	8.1
40.5	--	1.6	0.8	--
84.5	77	--	--	--
132.5	82	--	--	--

Hours at 75° F:	PFR-6 Resin	RS-375 Resin	Precoat[c]
1.1	--	--	4.5
17	1.1	0.1	--
23	--	--	6.4
84.5	3.2	0.7	--
90.5	--	--	7.6
132.5	3.4	0.5	--
Plus 72.5 Hours at 150° F	13.4	3.9	--

(a) Weight losses on three individual samples, exposed simultaneously, are averaged.

(b) This material, 4, 4'-diphenyl methane diisocyanate, is of interest as it is the diisocyanate resulting from the rearrangement of Structure X.

(c) Formulation containing small amount of plasticizing acetone (most volatile component), 20 wt. in % Structure I as wetted solids and the balance viscous low prepolymer of PFR-6 and tolylene diisocyanate.

B. Sublimation in High Vacuum Measurements

Measurements of weight losses sustained over multi-hour exposures to high vacuum at 75° F and 150° F of azides and polyol resins are reported in Table D. The troublesome volatility of azide Structure I is evident, but Structures X and XI appear much better. Resin PFR-6 appears to contain an appreciable amount of relatively volatile material and RS-375 quite a bit less. The weight losses from the precoat formulation (a two-phase material) are difficult to interpret but suggest an appreciable loss of a minor component (Structure I, the solid phase) may have occurred.

C. Foaming Studies

Work has continued on the problem of controlling foam cell structure in slow foaming in vacuum. Use of 0.5 per cent silicone additive L-5310 and vacuum foaming has given foam with a polymer melt temperature (PMT) on a hot bar of 340 to 360° F, employing an equivalence of Structure X and PFR-6 prepolymered about 30 per cent with tolylene diisocyanate (TDI). Some loss of azide or diisocyanate in the vacuum foaming probably occurred, for the same formulation in atmospheric pressure foamings exhibited a PMT from 370° F to above 460° F.

III. PROBLEM AREAS

The extension of the foam formulation effort in the revised plan (see Figure 1) has imposed a tight schedule in the testing effort. An extension of time may be necessary to complete the testing phase. However, this would not necessitate any additional funding.

IV WORK TO BE PERFORMED DURING THE NEXT REPORTING PERIOD

1. Inspections of azide structures will continue.

2. Evaluations of urethane resins and foams from the available azides and various resins or pre-polymered resins will be made.

3. Preparation will be attempted of more advanced pre-polymers to be evaluated as precoat ingredients. This with the objective of carrying the urethane polymerization process as far as possible before the final polymerization (and foaming) step which utilizes an azide. A reduction in the azide requirement is sought.

Figure 1
EAP 3-1206

PROGRAM SCHEDULE-RIGIDIZED INFLATABLE SOLAR ENERGY CONCENTRATORS - REVISION "A"

TASK	1963 OCT	NOV	DEC	1964 JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEPT
I. OPTIMIZATION OF RIGIDIZING MATERIAL												
A. Foam Formulation												
B. Sample Tests												
II. DETERMINATION OF MATERIAL CHARACTERISTICS												
A. Screening Tests												
B. Specimen Manufacture												
C. Specimen Tests												
1. Thermal Conductivity												
2. Linear Thermal Expansion												
3. Stress-Strain												
4. Poisson's Ratio												
5. Shear												
6. Bond Strength												
7. Creep												
8. Dimensional Stability												
9. Ultra-Violet Effects (Bond Strength & Stress-Strain)												
10. Reflectance												
D. Structural & Thermal Analysis												
III. FABRICATION & TESTING TWO-FOOT MODEL												
A. Model Rigidization												
IV. REPORTS												
MONTHLY	▲	▲	▲	▲	△	△	△	△	△	△	△	△
QUARTERLY			▲			△			△			
FINAL												△
V. PROJECT ENGINEERING & ADMINISTRATION												

Posting Dates
11-5-63
12-5-63
1-5-64
2-5-64

Legend
△ ▭ Projected Effort
▲ ■ Completed Effort
⬚ Scheduled To Complete